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SMR/382- 2

WORKSHOP ON SPACE PHYSICS:
"Materials in Micogravity"
27 February - 17 March 1989

"Some Sources of Defects in α - Hgl₂ the RoomTemperature
y-Ray Detector"

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Abstract

In the course of a systematic optimization of the materials properties of α -HgI₂ crystals for room temperature γ- and x-ray detectors, we have investigated possible sources of defects and discuss briefly the possibility to suppress them. Due to the particular structure of α -HgI₂, large amount of impurities particularly hydrocarbons can be absorbed in van der Waals layers and lattice channels. Purification by sublimation does not work due to the affinity of hydrocarbons to iodine and their easy re-absorption in the sublimate. "Lattice filtering" of the large concentration of hydrocarbons contained even in "suprapure" iodine has been performed using the close spaced lattice of CuI. Oxidation of hydrocarbons by reaction of oxygen with HgI₂ is another possibility for their removal.

Mass spectrometric investigations of a molecular beam of α -HgI₂ has solved the long disputed problem of the existence of nonstoichiometry: both excess of Hg or excess of I are possible. The removal of nonstoichiometry can be achieved by suitable thermal treatment only in the case of pure crystals. In the presence of hydrocarbons, the non-stoichiometric defects are fixed showing the predominant importance of hydrocarbons for α -HgI₂.

Investigation of the evaporation of α -HgI₂ with mass spectrometry at low temperatures ($150 > T > 40^\circ \text{C}$) shows a strong change of the enthalpy of evaporation at 67°C whereas DSC does not show any peak at this temperature. It seems probable that this is due to a surface reconstruction which influences the evaporation but not the thermal bulk lattice effects which are detected by DSC.

* Dedicated to Prof. Dr. K. L. Komarek at the occasion of his 60th birthday.

1. Introduction

α -HgI₂ is a very interesting material for room temperature semiconductor detectors of x- and γ-rays. The commercially available semiconductor detectors (Si and Ge) have a narrow band gap compared with the kT energy and, therefore, show at room temperature a strong thermal noise. Due to this reason they are used only at liquid nitrogen temperature. On the other hand, α -HgI₂ has a much larger band gap (2.13 eV) than the kT energy at room temperature. It is, therefore, used without cooling. This allows miniaturization and fabrication of arrays which can have large impact in many different fields of applications such as γ-spectrometers and -cameras, human tomography, nuclear medicine, EDAX detectors for scanning electron microscopes, portable analytic probes to be used for mineral prospecting etc..

In spite of its many and unique advantages α -HgI₂ detector crystals have also one drawback. They have a high concentration of traps which decrease the mobility, particularly of the positive charge carriers. These traps are attributed to crystal defects but nothing is known about their nature.

In the following we investigate the incorporation of impurities, nonstoichiometry and structural stability as possible sources of defects. An extensive review on the state of the art of α -HgI₂ crystals and detectors is under preparation now and will be published elsewhere [1].

2. Purity

Mass spectrographic investigations of organic [2] and inorganic [3] impurities have shown large concentrations for crystals of most important laboratories. Particularly important are the hydrocarbons which are introduced by iodine. Even the highest purity commercial iodine "suprapur" (Merck) shows a very high concentration of organic impurities (Fig. 1). The difficulty to separate the hydrocarbons is probably due to their affinity to iodine and the formation of iodinated derivatives.

The existence of hydrocarbons in the α -HgI₂ lattice is supported, besides of the mass spectrographic analysis, also by direct evidence: melting of single crystals purified by repeated sublimation still produces carbon skins due to pyrolysis of the hydrocarbons. Their omnipresence in α -HgI₂ is, therefore, accepted by now.

More difficult is to decide which lattice sites the long hydrocarbon molecules are occupying. The red α -HgI₂ modification, which is used for the detectors, is tetragonal and crystallizes in a layer structure with the space group P4₂/nmc. In principle, there are two related lattice sites which seem probable for the incorporation (intercalation) of long hydrocarbon molecules. The iodine double layers (001) with van der Waals bonding (Fig. 2, plexiglass plates) and the associated channel systems \parallel to a- and b-axis. The cross section of these channels and, therefore, their capacity for intercalation depends on the degree of ionicity of the Hg-I bonding. Very little is known about that [1]. The best guess at present is 30% ionicity [4]. This means that the channels are smaller than shown in the model of Fig. 2 (100% covalency) but have still a cross section, which in principle could allow intercalation of linear hydrocarbon chains.

To look for clues about the absorption sites for hydrocarbons, we have critically reviewed the lattice constants published in the literature. Figure 3 shows the values of c/a ratio. Although, appreciable variations appear in the c/a values between different laboratories (up to 0.7%), a clear cut picture is not existing. The results indicate rather that the van der Waals bonding is not particularly expanded. This would mean that the hydrocarbon chains are ^{incorporated} in the channels without influencing very much the interatomic distances of the iodine double layer.

An alternative model has been presented in the past [5], proposing that due to the incorporation of impurities distortion of the van der Waals layers takes place leading to the formation of mosaic structure. The impurities should be accumulated at the various grain boundaries. Ion probe measurements gave some support for this model [5]. Although we did not investigate similar crystals with those investigated by Huth [5], his model, plausible from several aspects, seems to contradict the possibility of solid solutions of hydrocarbons with α -HgI₂ and to support the case of precipitation. Our evaporation experiments, however, show clearly the change of evaporation enthalpy by hydrocarbon doping (Fig. 4), a thermodynamic proof of the existence of solid solutions.

Purification of α -HgI₂ is not complete due to the readsorption of the volatile hydrocarbons evaporating from the source on the sublimate. This is shown by the existence of carbonaceous skins on molten material heated near the boiling point (354° C) after repeated (up to 30x) sublimations in dynamic vacuum. By the way, this is not astonishing as thermodynamic calculations indicate tempe-

ratures = 1200° C for efficient pyrolysis of the hydrocarbons. Increase of the efficiency of purification from less volatile impurities by sublimation is achieved by leaving a residue of 1/4 of the starting charge in the source zone.

Based on the results of our earlier work [2] we have purified iodine by introducing it in a close packed lattice, such as that of CuI. The underlying idea is that the strong absorption of hydrocarbons in α -HgI₂ is related with its structure. In a close packed structure no large enough sites are available for incorporation of large organic molecules. Using a hydrocarbon-free glass-metal UHV system with mercury pumps, CuI was synthesized from spectroscopically pure copper and "suprapur" iodine (Merck) which has been twice sublimated [6,7]. Purification in the same apparatus by repeated dynamic sublimations transformed the originally gray-black reaction product, which was mixed with many black carbon skins, to a yellow and then almost white material. Zone melting or crystal growth from the vapor led to clear crystals. Decomposition of the crystals under dynamic vacuum at 750° C (in the above UHV-apparatus) produced hydrocarbon-free iodine which was reacted in situ with mercury to α -HgI₂. The purity of this iodine could be checked indirectly by sparse source mass spectrographic analysis of the CuI crystals. They contained 1/10 of the total hydrocarbon concentration of the purest HgI₂ crystals grown from material synthesized by repeatedly sublimated iodine. This result supports the idea that the structure of α -HgI₂ is to a large degree responsible for the high content of hydrocarbons.

Another method of purification is oxidation of hydrocarbons in HgI₂. Thermodynamic calculations show that the equilibrium constants for such reactions are orders of magnitude higher than those for pyrolysis. On the other hand, HgO and I₂O₅ decompose to the elements at T > 300° C. Preliminary experiments in sealed ampoules filled with HgI₂ and 100 Torr O₂ showed that at source temperature 600° C and vapor temperature 1000° C no carbon skins are formed. In fact it was possible to use this material for crystal growth, leaving only a small yellow residue at the source.

Work is continued now to produce larger quantities of pure material for crystal growth of large crystals and detector fabrication. Only then the importance of impurities for the detector properties would be definitely clarified. Presently only indications are existing for the detrimental influence of impurities. Thus, increasing degree of purity of the source material over the

years has clearly enhanced the quality of the detectors. On the other hand, thin crystal platelets grown under very high supersaturation in the presence of appreciable hydrocarbon concentration (few Torr) [8-11] have very good detector properties. Presently, it is very difficult to explain this behavior. Investigations of the nonstoichiometry of such platelets by mass spectrometry of a molecular beam (compare sect. 3) [6] showed that in addition to an appreciable amount of hydrocarbons these platelets contain excess Hg. The latter is known to increase the mobility of electrons. As in the applications of the platelets (x-ray, EDAX detectors) the low mobility of holes is not so important, the increased mobility of electrons combined with stabilization of certain defects due to the presence of hydrocarbons (sect. 3) may explain the good detector properties of the "dirty" platelets. This is only one example of the complexity of the α -HgI₂ properties.

3. Nonstoichiometry: Molecular Beam Studies

There is only one study on the phase diagram of the system mercury - iodine by Dworsky and Komarek [10] (Fig. 5). Eleven years later the nonstoichiometry of HgI₂ has been one of the most disputed aspects of α -HgI₂, as several laboratories have presented contradicting evidence about its existence and excess component [11-13]. As wet chemical analysis at the limit of its accuracy has been used in these works [11-12] it became clear that other methods of investigations are necessary.

To answer in a semi-quantitative way the question of nonstoichiometry in α -HgI₂ we have used the mass spectrometric analysis of a molecular beam resulting from evaporation of α -HgI₂ single crystals [6,14]. The underlying idea is that if the crystals contain the nonstoichiometric component, this could be sensitively detected, particularly since we have shown (sect. 4) that molecular evaporation of HgI₂ takes place. In case of incongruent evaporation (preferential evaporation of one component) our goal could be achieved only if total evaporation experiments are performed and the ratio of the components in the resulting ion beam is monitored till the last grain has evaporated in the effusion cell.

The results of our investigations [6] showed clearly that nonstoichiometry towards both components is in principle possible (Hg- or I-excess). The direct thermodynamic proof is given by the appreciable changes (up to 33%) of the enthalpy of evaporation found in crystals with various nonstoichiometry and doping (Fig. 4).

3.a Excess Mercury; Sensitivity of the Determination

Excess of mercury could be easily shown from the "clastograms" (sect. 4) which give the relative abundance of the various ions as a function of the ionization energy. Figure 6a shows the clastogram of a Hg-rich sample. The excess Hg is easily seen if we compare with a stoichiometric sample (Fig. 6b). With decreasing ionization energy the Hg⁺-signal (in %) in Fig. 6a decreases, indicating that it is a fragment produced by the electron bombardment of HgI₂⁺, which is the parent ion (sect. 4). On the contrary, decreasing voltage leads to increase of Hg⁺ concentration in Fig. 6a, indicating that in this case Hg⁺ is also a parent ion resulting from the ionization of Hg vapor.

Based on this, we can estimate the sensitivity of determination of the excess component. The contribution of the Hg⁺ fragment ions in the total ion current at 70 eV (the standard ionization energy) is $40 \pm 5\%$ and that of I₂⁺ fragment $1.5 \pm 0.3\%$. These are averages of four measurements made with different samples of the same batch of pure and stoichiometric crystals. Accordingly, we can estimate the lower limit of detection of mercury and iodine vapors to be equal to 10% and 0.5% of the total ion current, respectively. We conclude, therefore, that the sensitivity of detection is 1% of the equilibrium vapor pressure for mercury and $10^{-3}\%$ of the equilibrium vapor pressure for iodine.

From the point of view of the preparation of stoichiometric samples it is interesting to note that the heat treatment leads to slow desorption of the excess component. This is clearly shown by monitoring all relevant ion masses during a total evaporation experiment (Fig. 7a). From these data the ratio $(I/Hg)_{ion}$ in the ion beam can be calculated as a function of time (Fig. 7b). It should be noted that the absolute value of this ratio does not represent directly the vapor stoichiometry, since it depends not only on the vapor composition but also on other factors (kinetics of the fragmentation reactions, ionization energy, mass discrimination at particular ion source and photomultiplier). However, the relative changes of this ratio show changes of the stoichiometry of the evaporating crystals. The absolute values of the $(I/Hg)_{ion}$ can be calibrated for a given ion source from samples of known stoichiometry. For pure sample C, which showed neither excess of Hg nor that of I (Fig. 6) the constant value $(I/Hg)_{ion} = 1.0$ has been measured. Figure 7 shows, therefore, that an initially Hg-rich sample - $(I/Hg)_{ion} = 0.6$ - loses the excess component after 5 1/2 hours and suddenly becomes stoichiometric $(I/Hg)_{ion} = 1.0$. This means that nonstoichiometric material can be made stoichiometric by evaporation in a semi-open system. However, about 40% of the material must evaporate in order that the total amount of the excess mercury is expelled.

3.b Excess Iodine

The evaporation of the excess iodine is even more rapid, so that the time necessary for a clastogram is not available. In this case the Arrhenius plot of the (ion current x temperature) product gives the direct proof of the existence of the nonstoichiometry. Figure 8 shows these plots for the first run (curve 1) and the second run (curve 2). As it can be seen, in the first run the I_2^+ signal was 20x larger than for stoichiometric material. However, even the largest signal (at 80° C) was 10^4 times smaller than that corresponding to the equilibrium vapor pressure of solid iodine. Thus, we have the thermodynamic verification that no free iodine was present in the crystal. On the other hand, the slope of curve 1 ($\Delta H = 20.4 \pm 2.6$ kcal/mol) is too large for chemisorption. We conclude, therefore, that the iodine is dissolved or intercalated in the lattice. Instead of the more or less isothermal jump of the Hg^+ signal (Fig. 7), the evaporation of the excess iodine shows a depletion range of approx. 30° C (Fig. 8). After that, the evaporation follows the partial pressure of a stoichiometric sample. We conclude that excess iodine evaporates preferentially at lower temperature than excess mercury.

3.c Nonstoichiometry in the Presence of Hydrocarbons

The above conclusions apply only to hydrocarbon free HgI_2 . Presence of hydrocarbons changes the situation completely. Figure 9 shows the case of HgI_2 platelets grown in the presence of organic additives. Complex hydrocarbon spectra are found in the molecular beam (insert). The strongest signal 59^+ has been also monitored during total evaporation (Fig. 9a).

Most instructive is the behavior of the $(I/Hg)_{ion}$ ratio. Anomalies during the slow heating period are followed by a steady state with $(I/Hg)_{ion} < 1.0$ indicating excess mercury. No change of the stoichiometry takes place like in case of Fig. 7 where the Hg-excess is exhausted after 3h of isothermal heating. We conclude, therefore, that presence even of small amounts of hydrocarbons is stabilizing the nonstoichiometric excess component. This indicates that annealing of the nonstoichiometric defects and removal of the corresponding traps is not possible in the presence of hydrocarbons.

4. Phase Stability

The clastogram of pure and stoichiometric material (Fig. 6) shows that the sole thermodynamically stable species in the evaporation reaction is HgI_2 . It is only the HgI_2^+ ion whose percentage increases strongly with decreasing ionization energy. We conclude, therefore, that the evaporation reaction is molecular (non-dissociative) [14]:



Fig. 10 shows the vapor pressure curve as measured mass spectrometrically with a QMG-511 (Balzers AG) quadrupole mass spectrometer with cross-beam ion source and off-axis photomultiplier. A hydrocarbon-free UHV apparatus has been used. For background discrimination the molecular beam has been chopped [14]. Calibration with Hg (curve a, Fig. 10) allowed the calculation of the vapor pressure data.

As the best crystals for detectors are grown from the vapor phase, the evaporation study is important both in order to measure the thermodynamic data and also to investigate fields of stability of the various HgI_2 modifications. Particular attention has been given to the range of temperatures lower than the crystal growth temperature ($T = 110^\circ$ C), which have not been investigated up to now. Thus the investigation was extended from 150° C down to 40° C. This temperature range is very important because defects formed at $T < 80^\circ$ C probably cannot be removed from the crystals and will influence the detector performance. The calibrated vapor pressure curve c in Fig. 10 shows unexpectedly not only the enthalpy change at the transition $\alpha \rightarrow \beta$ - HgI_2 at 127° C but also a strong change of the slope at 67° C. This is shown with much better statistic in curve b which has been measured with a noncalibrated effusion cell. The corresponding evaporation enthalpies are

$$\begin{array}{ll} T < 67^\circ \text{ C} & \Delta H_{1ev} = 15.0 \pm 0.6 \text{ kcal/mol} \\ 67^\circ \text{ C} < T < 127^\circ \text{ C} & \Delta H_{2ev} = 26.4 \pm 0.8 \text{ kcal/mol} \\ T > 127^\circ \text{ C} & \Delta H_{3ev} = 20.17 \pm 0.8 \text{ kcal/mol} \end{array}$$

We note the large change of enthalpy at 67° C (42%) and the decrease of the absolute value leading to an increase of the vapor pressure at lower temperatures and increase of entropy.

α - HgI_2 is a material with very complex properties. It is, therefore, too early to draw final conclusions about the nature of this effect. On the other hand, it is important to consider possible explanations supported by already existing experimental evidence. To find out if the enthalpy change at 67°C is the result of a bulk structural transition (like that at 127°C) we have investigated a single crystal with differential scanning calorimetry (DSC). Although the $\alpha \rightarrow \beta$ transition at 127°C gave a very strong signal, no signal appeared at 67°C . Our present interpretation is that a surface reconstruction could take place at this temperature. Change of the surface structure will influence the evaporation process but will not have measurable influence on the bulk thermal properties measured by DSC. As mentioned above, a surface reconstruction at a temperature lower than the growth temperature and much lower than the m.p. ($T_{\text{tr}} = 0.6 T_{\text{m.p.}}$) will be the source of a high concentration of defects. This is in very good agreement with the findings of the detector industry [15], that a surface layer of the as grown crystals - which usually has higher perfection than the bulk of the vapor grown crystals - contains a high concentration of defects.

The existence of a surface phase with different structure on α - HgI_2 near room temperature has been recently reported as the result of x-ray investigations [16]. These authors report the disappearance of the α - HgI_2 reflections of freshly grinded powders after 12 hrs. A few other reflections grow at the same time, which the authors attribute to the yellow β - HgI_2 (orthorhombic) modification. As the penetration depth of the x-rays in the strongly absorbing HgI_2 is small (few micrometers), the authors report that this transition takes place only on a surface layer, the core of the powder grains retaining the red α - HgI_2 modification. The experimental evidence for this surface phase transition is quite convincing. What, however, is not clear is the assignment of the orthorhombic structure based on very few reflections. A survey of the literature shows that the modification which would support both our results and those of Long et al. [16] is the orange modification [17]. It has been grown by sublimation from 130 to 70°C [18] and its thermal stability range is reported to be $T < 60$ - 70°C [19]. This phase is reported as metastable in the sense that under the smallest mechanical pressure it transforms to α - HgI_2 . As no mechanical pressure is applied in the effusion cell, it is possible that it can be formed on the surface of α - HgI_2 crystals.

5. Conclusions

Large concentration of impurities, nonstoichiometry and surface instability at 67°C , seem to be sources of defects in α - HgI_2 . Therefore, the high concentration of defects in the detectors is not astonishing. As a matter of fact astonishing is rather that some very good detectors of spectrometer quality can be still made from this material. Although a one-to-one relationship between such defects and the electronic traps in the detectors has not yet been found due to lack of systematic investigations on well characterized crystals, it is expected that at least some of these defects act as traps.

According to our investigations, the removal of the defects resulting from impurities and nonstoichiometry should be achieved when hydrocarbon-free, pure starting material is available for crystal growth. The detrimental influence of the surface reconstruction is limited in a not very thick surface layer which can be mechanically removed.

Another source of defects which has not been discussed here is due to mechanical distortion of the material. This has been investigated several times in the past [20]. We only note here, that very large α - HgI_2 ($> 500\text{ g}$) tend to deform under their own weight, so that ideal conditions for the growth could be found in space. The results of the Spacelab-3 experiment [21] fully confirm this conclusion.

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Figure captions

Fig. 1 Mass spectrum of iodine "suprapur" (Merck) measured by a gas chromatography-mass spectrometry technique. (The measurement has been performed in Laboratoire de Spectrometrie de Masse, Université de Genève).

Fig. 2 A view of the α -HgI₂ layer structure along the a- (or b-)axis. (This model made from ping-pong balls does not take into account the slightly different size of I- and Hg-atoms) A system of channels along a- (or b-)axis is clearly seen. The plexiglass plates separate the neighbouring sheets of [HgI₄] tetrahedra and show the regions with van der Waals bonding.

Fig. 3 Ratio of the lattice constants c/a of α -HgI₂ reported in the literature since 1950.

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Fig. 4 Variation of the sublimation enthalpy of mercuric iodide with the purity and non-stoichiometry of HgI_2 samples.

- A - mercury-rich HgI_2 , synthesized from "suprapur" mercury (Merck) and pro analysis iodine (Merck).
- B - iodine-rich HgI_2 , synthesized as A.
- C - pure HgI_2 , synthesized in vacuum from mercury "suprapur" and iodine from decomposition of CuI .
- D - hydrocarbon-doped HgI_2 , formerly synthesized from the "suprapur" elements.
- E - iodine-doped HgI_2 ; formerly synthesized from the "suprapur" elements.
- F - platelets of HgI_2 grown in the presence of organic additives.

Fig. 5 Phase diagram of the system $\text{Hg}-\text{I}_2$. (After Dworsky and Komarek [10])

Fig. 6 a The relative abundance of the ions vs. ionization energy (clastogram) for the mercury-rich sample F (see caption Fig. 4). Mass spectrometric measurements.

Fig. 6 b The relative abundance of the ions vs. ionization energy (clastogram) for the stoichiometric sample C (see caption to Fig. 4). Mass spectrometric measurements.

Fig. 7 Change in ion current of the major ions (a), temperature and $(\text{I}/\text{Hg})_{\text{ion}}$ ratio (b) in the ion beam as a function of time during the total evaporation of sample A (Hg-rich).

Fig. 8 Temperature dependence of HgI_2^+ and I_2^+ ion current for the sample B (see caption to Fig. 4). Rings - 1st heating; rectangles - 2nd heating.

Fig. 9 Change in ion current of the major ions (a), temperature and $(\text{I}/\text{Hg})_{\text{ion}}$ ratio (b) in the ion beam as a function of time during the total evaporation of sample F (HgI_2 platelets; see caption to Fig. 4). In the insert the mass spectrum of organic impurities in this sample is shown.

Fig. 10 Temperature dependence of the vapor pressure of mercury (curve a) and mercuric iodide (curve b). Curve b was measured with a non-calibrated Knudsen cell, thus its absolute pressure is not known.













